RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2017, 7, 44333

Received 2nd September 2017
Accepted 8th September 2017

DOI: 10.1039/c7ra09770k

rsc.li/rsc-advances

Annulation of 2,3-diphenyl-4*H*-chromen-4-ones *via* photo-induced hydrogen evolution†

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An efficient photo-induced transition-metal-free direct hydrogen evolution and annulation of 2,3-diphenyl-4*H*-chromen-4-ones in EtOH–H_2O (19 : 1, v/v) at room temperature was described. The reported methodology provided a quick and easy access to the synthesis of dibenzo[*a*,*c*]xanthen derivatives, which eliminates the use of any catalysts, oxidants and additives.

Introduction

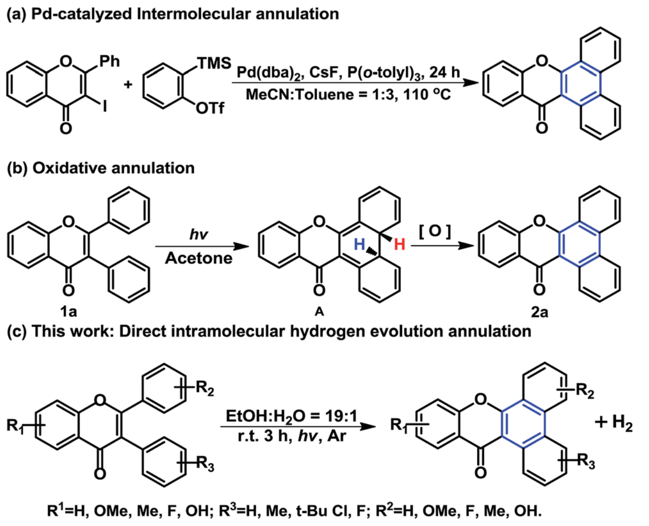
In recent years, photochemical reactions have drawn great attention due to their environmentally friendly properties, sustainability and high atom efficiency compared to conventional transition-metal catalyzed reactions.[1,2] Furthermore, photons have been recognized as an ideal clean reagent for organic reactions.[3,4] Photochemical reactions have been successfully applied to the synthesis of phenanthrene derivatives and polycyclic aromatic hydrocarbons (PAHs),[5,6] which are difficult to achieve *via* traditional chemical conditions.

Chromones are the core structures of flavonoids and isoflavonoids and have been extensively studied as biologically active substrates as well as drug molecules.[7,8] Owing to their tremendous significance in biological and pharmaceutical activities,[9] great effort has been made in the development of various chromone derivatives. Recently, transition-metal catalyzed C–H activation and annulation have been successfully applied for the synthesis of polycyclic derivatives of chromones. Yoshikai *et al.* reported $Pd(dba)_2$ catalyzed cyclization of 3-iodoflavones with 2-(trimethylsilyl)phenyl triflate in the presence of CsF and $P(o\text{-tolyl})_3$ at 110 °C for 24 h to give dibenzo[*a*,*c*]xanthen derivative **2a** in 79% (Scheme 1a).[10]

Alternatively, the irradiation of 2,3-diphenyl-4*H*-chromen-4-one **1a** in acetone with a medium pressure mercury lamp under the air atmosphere for 1 h yielded trace amount of **2a** (5%, Scheme 1b).[11] It was proposed that **2a** was generated *via* the well-known stilbene-phenanthrene type photocyclization of 2,3-diphenyl-4*H*-chromen-4-one **1a.** Generally speaking, photocyclization of stilbene analogues always require the presence of oxidant (O_2 or I_2, KI, $CuCl_2$, TCNE *et al.*) for the reaction to proceed smoothly.[12–14] Luckily, we were able to obtain the cyclization products of 2,3-di(hetero)aryl-4*H*-chromen-4-ones without the requirement of any oxidant or additives.[15] However, the annulation product for less reactive 2,3-diphenyl-4*H*-chromen-4-one substrate was not obtained. Following our investigation in the development of photo-induced transition metal-free cross-coupling reaction[16] as well as the direct oxidative annulation,[15,17,18] we would like to extend an efficient photo-induced intramolecular hydrogen evolution and annulation to 2,3-diphenyl-4*H*-chromen-4-ones substrate, which provides access to dibenzo[*a*,*c*]xanthen analogues (Scheme 1c).

Results and discussion

Initially, the photo-induced oxidative annulation of 2,3-diphenyl-4*H*-chromen-4-one (**1a**) was optimized and the



Scheme 1 Synthetic approaches to dibenzo[*a*,*c*]xanthenes.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra09770k

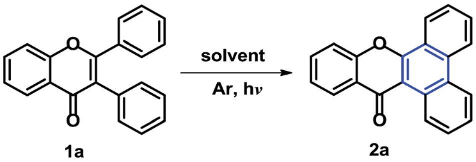
corresponding data were presented in Table 1. Thus, irradiation of **1a** in acetonitrile (100 mL) with a 500 W high-pressure mercury lamp at ambient temperature under argon atmosphere for 3 h gave **2a** in the yield of 49% (entry 1). Annulation of **1a** in acetone or dichloromethane did not improve the yield of **2a** (38–43%, entries 2–3). While, similar yield of **2a** was obtained in ethanol (56%, entry 4). It was interesting to find out that the yields of **2a** were significantly affected with the presence of H_2O (entries 5–8). The amount of additional water played a critical role towards the cyclization, since **2a** was obtained in lower yields with either too much or too little water. The optimal yield was obtained when $EtOH/H_2O$ (19 : 1, v/v) was chosen as solvent (63%, entry 7). Meanwhile, the concentration of **1a** was also explored (entries 7, 9–10) and **2a** was obtained in highest yield when the reaction was performed in 5 mM scale (63%, entry 7). Finally, screening of irradiation time was conducted and lower yield of **2a** was obtained (entries 11–12). When the cyclization was performed under open air, **2a** was obtained in 32% yield (entry 13). Thus, the irradiation of 5 mM **1a** in EtOH–H_2O (19 : 1, v/v) at ambient temperature for 3 h under the argon atmosphere was determined to be the optimal condition.

With the optimized conditions in hand, the tolerance of various functional groups (methyl, *tert*-butyl, fluoro, chloro, hydroxyl and methoxyl) has been explored and the yields were summarized in Table 2. Generally speaking, the substrates bearing electron-donating groups (*e.g.*, Me, OMe, *t*-Bu) gave the corresponding products **2a–2p** in higher good yields (59–81%) comparing to those (**2q–2x**, 54–69%) bearing electron-withdrawing groups (*e.g.*, F, Cl). Notably, the substrates bearing free hydroxyl group also yielded the corresponding annulation products **2y** and **2z** in high yields, which are better than the yields of **2l** and **2e**, respectively. There is a significant difference in the irradiation time as well. Substrates containing EWG usually require longer reaction time than those with EDG. The structures of 2 were characterized by ^{1}H NMR, ^{13}C NMR, HRMS and IR.

Based on our experimental data and a literature report,[19] a plausible mechanism for the formation of **2a** is depicted in Scheme 2. Initially, the irritation of 2,3-diphenyl-4*H*-chromen-4-one (**1a**) with a high-pressure mercury lamp generate intermediate A, followed by a thermal suprafacial [1,5]-H shift[20] to give intermediate B. Spontaneous rearomatization of benzene ring is believed to be the force driving for [1,5]-sigmatropic shift. Subsequently, keto–enol isomerization of B led to the formation of a more stable *syn*-isomer C. Similar transformations have been reported for a number of structurally related compounds.[15,21–24] It is worth mentioning that polar protic solvent EtOH–H_2O (19 : 1, v/v) plays an important role in the process of keto–enol isomerization, which accounts for higher yields of **2a** comparing to MeCN, $CHCl_2$ and Me_2CO. In the end, the annulation product **2a** was obtained along with the elimination of hydrogen molecule *via syn*-elimination from intermediate C, which could be easily explained by the restoration of aromaticity for the benzene ring and the entire conjugated system. To our delight, we have successfully detected the hydrogen *via* GC and the detail experiment was shown in ESI-Fig. 2.† The annulation product **2a** was also produced under the open air (oxygen, Table 1, entry 13), and it indicated that the photochemical cyclization proceed through the S1 state.

Encouraged by the further certified the proposed mechanism, we turned our attention to the reductive carbonyl. **1a** was reduced to **3** under the presence of $LiAlH_4$ $AlCl_3$ in THF at 0 °C for 30 min to gave **3** (yield 44%, Scheme 3).[25] As expected, no

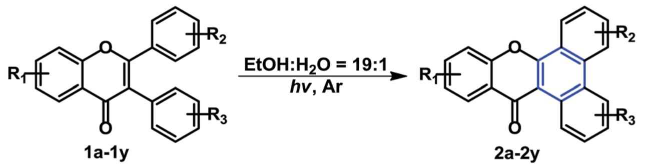
Table 1 Optimization for the annulation of **1a**[a]



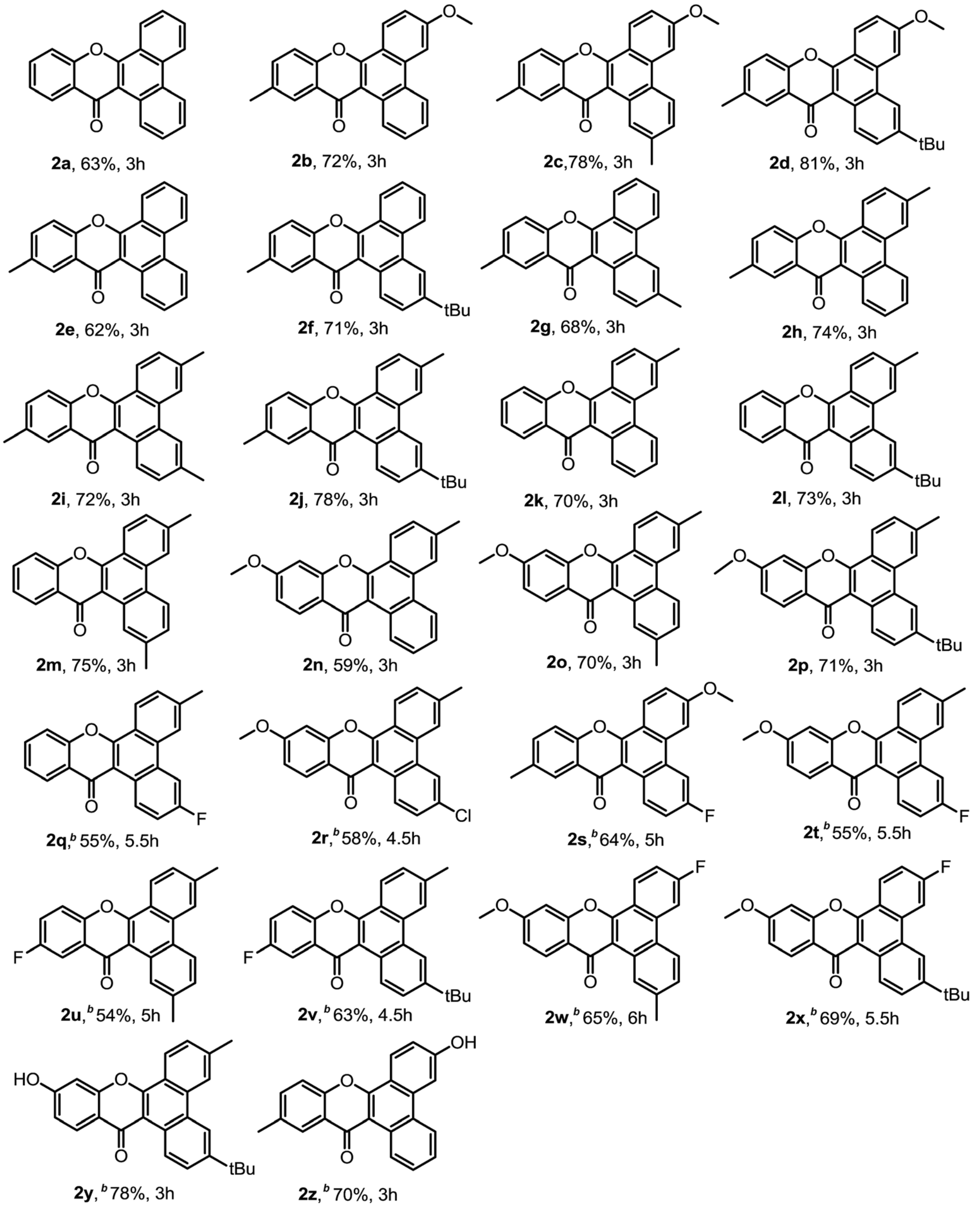
Entry	Concn (mM)	Solvent (v/v)	Time (h)	Conv[b] (%)	Yield[b] (%)
1	5	MeCN	3	73	49
2	5	Me_2CO	3	69	38
3	5	CH_2Cl_2	3	64	43
4	5	EtOH	3	75	56
5	5	EtOH–H_2O (7 : 1)	3	83	38
6	5	EtOH–H_2O (13 : 1)	3	72	45
7	**5**	**EtOH–H_2O (19:1)**	**3**	**94**	**63**
8	5	EtOH–H_2O (25 : 1)	3	71	49
9	3	EtOH–H_2O (19 : 1)	3	96	37
10	7	EtOH–H_2O (19 : 1)	3	70	41
11	5	EtOH–H_2O (19 : 1)	5	100	51
12	5	EtOH–H_2O (19 : 1)	1	54	36
13	5	EtOH–H_2O (19 : 1)	3	79	32[c]

[a] 0.5 mmol **1a** in various solvent (100 mL, 5 mM) was irradiated with a 500 W high-pressure mercury lamp at room temperature in the argon atmosphere. [b] Isolated yield. [c] In the open air atmosphere.

Table 2 Substrate scope[a]



1a-1y → **2a-2y**



2a, 63%, 3h; **2b**, 72%, 3h; **2c**,78%, 3h; **2d**, 81%, 3h

2e, 62%, 3h; **2f**, 71%, 3h; **2g**, 68%, 3h; **2h**, 74%, 3h

2i, 72%, 3h; **2j**, 78%, 3h; **2k**, 70%, 3h; **2l**, 73%, 3h

2m, 75%, 3h; **2n**, 59%, 3h; **2o**, 70%, 3h; **2p**, 71%, 3h

2q,[b] 55%, 5.5h; **2r**,[b] 58%, 4.5h; **2s**,[b] 64%, 5h; **2t**,[b] 55%, 5.5h

2u,[b] 54%, 5h; **2v**,[b] 63%, 4.5h; **2w**,[b] 65%, 6h; **2x**,[b] 69%, 5.5h

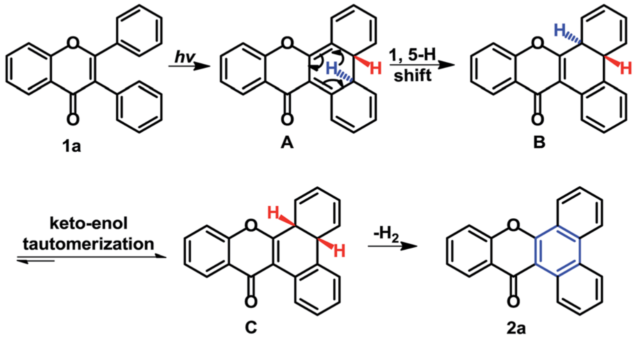
2y,[b] 78%, 3h; **2z**,[b] 70%, 3h

[a] All reactions were carried out on the 0.5 mmol scale with the irradiation of 500 W high-pressure mercury lamp under the argon atmosphere at room temperature until substrate was completely consumed (TLC monitor). [b] The yields of **2q–2x** was 39%, 45%, 49%, 31%, 46%, 40%, 43%, and 55%, for 3 h, respectively.

annulation product **4** was detected at the optimal reaction conditions, which could be explained to the lack of keto–enol tautomerization.

Conclusions

In summary, we have demonstrated a simple photo-induced direct hydrogen evolution and annulation for the synthesis of



Scheme 2 Proposed reaction mechanism for the formation of **2a**.

14*H*-dibenzo[*a*,*c*]xanthen-14-one derivatives in 95% EtOH under room temperature. Comparing to conventional transition-metal-catalyzed annulation and oxidative photo-cyclization reaction, the reported methodology offers several notable advantages, including simple operation, mild reaction condition, no catalysts, oxidants and additives. Meanwhile, the failure of the cyclization of **3** and detection the H_2 generated by the annulation of **1n** sufficiently proved the rationality of the proposed mechanism.

Experimental sections

Unless otherwise noted, commercial reagents were purchased from Energy Chemical. All experiments were determined by thin layer chromatography (TLC). TLC used silica gel 60 GF254 plate. Column chromatography (200–300 mesh) was performed on silica gel. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 or 600 MHzspectrometer. ^{1}H and ^{13}C NMR spectra were reported in parts per million (ppm) and referenced to the residual solvent peaks [$CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50)] for ^{1}H NMR and the $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52) for ^{13}C NMR spectra. High-resolution mass spectra (HRMS) were obtained using the electron-spray ionization (ESI) technique. Melting points were measured with a X-5 micro-melting point apparatus and were uncorrected. IR spectra were recorded with a Nicollet 170SX FT-IR spectrophotometer with KBr pellets. According to the literature reported for the synthesis of 3-iodo-2-phenyl-4*H*-chromen-4-one, which using 2-phenyl-4*H*-chromen-4-ones (1 mmol), I_2 (304 mg, 1.2 mmol) and $Ce(NH_4)_2(NO_3)_6$ (603 mg, 1.1 mmol) as starting materials and pre-dried MeCN (10 mL) as solvent a series of 3-iodoflavonoids compounds was obtained.[26]

General procedure for the synthesis of compounds 2a–2z

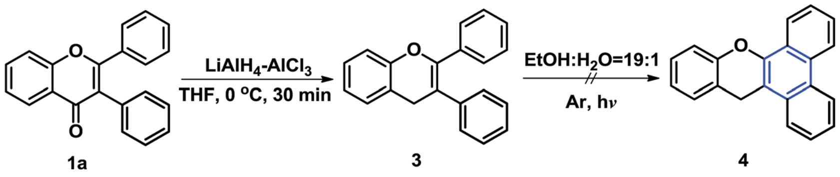
Substrate 2,3-diphenyl-4*H*-chromen-4-one **1a** (149 mg, 0.5 mmol) was dissolved in EtOH–H_2O (100 mL, 19 : 1, v/v) at ambient temperature in a quartz tube, and was degassed for 5 min *via* ultrasound, deaerated for 20 min by bubbling argon and irradiated with a high pressure mercury lamp (500 W) at room temperature for 3 h. Then the reaction mixture were removed under reduced pressure and purified by column chromatography (ethyl acetate/petroleum ether, 1 : 50) to give **2a** (63%).

14*H*-dibenzo[*a*,*c*]xanthen-14-one (2a).[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (d, J = 8.4 Hz, 1H), 8.77 (d, J = 8.2 Hz, 1H), 8.68 (t, J = 8.5 Hz, 2H), 8.46 (d, J = 7.9 Hz, 1H), 7.87–7.68 (m, 6H), 7.51–7.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.33, 155.21, 154.42, 133.92, 133.80, 130.62, 128.99, 128.57, 127.75, 127.50, 127.32, 126.71, 126.68, 124.71, 124.10, 123.99, 123.97, 122.90, 122.32, 117.50, 112.70.

6-methoxy-12-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2b). White solid. Yield: 72%, M_p: 229.3–231.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (d, J = 8.4 Hz, 1H), 8.42 (dd, J = 8.4, 5.7 Hz, 2H), 8.14 (s, 1H), 7.82 (d, J = 2.3 Hz, 1H), 7.69 (dd, J = 11.3, 4.1 Hz, 1H), 7.63–7.53 (m, 1H), 7.48 (dd, J = 8.5, 2.0 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.17 (dd, J = 9.0, 2.4 Hz, 1H), 3.97 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.10, 161.54, 155.33, 152.54, 135.81, 134.79, 134.36, 129.75, 128.62, 127.84, 126.85, 126.22, 125.96, 123.59, 122.27, 117.97, 117.18, 116.91, 110.89, 104.35, 55.57, 21.18; IR (KBr), ν (cm^{-1}) 2927, 1610, 1446, 1247, 1029, 925, 821, 628, 530; HRMS (ESI): calc. for $C_{23}H_{16}O_3$ [M + H]$^+$ 341.1178, found 341.1177.

6-Methoxy-2,12-dimethyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2c). White solid. Yield: 78%, M_p: 222.4–224.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.45 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.15 (s, 1H), 7.81 (s, 1H), 7.50–7.38 (m, 3H), 7.17 (d, J = 9.0 Hz, 1H), 3.99 (s, 3H), 2.60 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.20, 161.59, 155.54, 152.61, 138.68, 135.97, 134.74, 134.32, 129.82, 127.75, 127.63, 125.98, 124.71, 123.67, 122.20, 117.65, 117.20, 116.57, 110.83, 104.14, 55.57, 22.22, 21.21; IR (KBr), ν (cm^{-1}) 3101, 2914, 1612, 1442, 1238, 1130, 1029, 827, 622, 495; HRMS (ESI): calc. for $C_{24}H_{18}O_3$ [M + H]$^+$ 355.1334, found 355.1336.

3-(*tert*-Butyl)-6-methoxy-12-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2d). Yellow solid. Yield: 81%, M_p: 255.6–258.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (d, J = 8.9 Hz, 1H), 8.60 (d, J = 8.9 Hz, 1H), 8.51 (d, J = 2.3 Hz, 1H), 8.20 (s, 1H), 8.01 (d, J = 2.3 Hz, 1H), 7.83 (dd, J = 8.9, 2.0 Hz, 1H), 7.51 (d, J = 2.8 Hz, 2H), 7.28 (dd, J = 9.1, 2.4 Hz, 1H), 4.05 (s, 3H), 2.50 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.21, 161.58, 155.19, 152.77, 149.03, 136.20, 134.80, 134.37, 127.69, 127.53, 126.93, 126.74,



Scheme 3 Reductive carbonyl and attempt annulation of **3**.

126.22, 126.09, 123.73, 118.36, 118.16, 117.27, 116.16, 111.13, 105.19, 77.48, 77.16, 76.84, 55.68, 35.15, 31.60, 21.18; IR (KBr), ν (cm^{-1}) 2941, 1623, 1396, 1259, 1168, 1047, 854, 800, 576; HRMS (ESI): calc. for $C_{27}H_{24}O_3$ [M + H]$^+$ 397.1804, found 397.1804.

12-Methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2e). White solid. Yield: 62%, M_p: 251.9–254.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.20 (d, $J = 8.3$ Hz, 1H), 8.76 (d, $J = 8.3$ Hz, 1H), 8.68 (dd, $J = 12.8$, 8.3 Hz, 2H), 8.23 (s, 1H), 7.84 (dd, $J = 11.2$, 4.0 Hz, 1H), 7.78–7.72 (m, 2H), 7.69 (dd, $J = 11.2$, 4.0 Hz, 1H), 7.60–7.55 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.51, 155.25, 152.78, 135.17, 134.68, 133.96, 130.63, 129.24, 128.64, 127.88, 127.56, 127.39, 126.70, 126.12, 124.22, 124.18, 123.75, 122.98, 122.42, 117.38, 112.70, 21.21; IR (KBr), ν (cm^{-1}) 3045, 2960, 1739, 1629, 1487, 1392, 1271, 1037, 804, 719, 518; HRMS (ESI): calc. for $C_{22}H_{14}O_2$ [M + H]$^+$ 311.1072, found 311.1071.

3-(*tert*-Butyl)-12-methyl-14-*H*-dibenzo[*a*,*c*]xanthen-14-one (2f). White solid. Yield: 71%, M_p: 208.3–211.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (d, $J = 8.9$ Hz, 1H), 8.56 (d, $J = 8.3$ Hz, 2H), 8.49 (d, $J = 7.7$ Hz, 1H), 8.07 (s, 1H), 7.79 (dd, $J = 8.9$, 1.9 Hz, 1H), 7.72–7.65 (m, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.40–7.33 (m, 2H), 2.42 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.20, 154.60, 152.56, 149.11, 134.82, 134.29, 133.91, 130.21, 127.52, 127.14, 126.96, 126.77, 126.58, 125.88, 124.05, 123.50, 122.63, 118.10, 117.23, 112.46, 35.14, 31.58, 21.10; IR (KBr), ν (cm^{-1}) 3060, 2952, 1635, 1488, 1398, 1284, 1124, 1033, 923, 806, 763, 636, 522; HRMS (ESI): calc. for $C_{26}H_{22}O_2$ [M + Na]$^+$ 389.1517, found 389.1514.

3,12-Dimethyl-14-*H*-dibenzo[*a*,*c*]xanthen-14-one (2g). White solid. Yield: 68%, M_p: 231.8–233.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (d, $J = 8.6$ Hz, 1H), 8.75 (dd, $J = 8.2$, 1.0 Hz, 1H), 8.69 (d, $J = 8.3$ Hz, 1H), 8.46 (s, 1H), 8.23 (s, 1H), 7.86–7.80 (m, 1H), 7.76–7.70 (m, 1H), 7.62–7.55 (m, 3H), 2.63 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.57, 154.69, 152.87, 136.41, 135.13, 134.59, 133.80, 130.49, 130.22, 127.75, 127.72, 127.28, 126.89, 126.13, 124.33, 124.23, 123.76, 123.01, 122.41, 117.41, 112.73, 21.99, 21.22; IR (KBr), ν (cm^{-1}) 2910, 1930, 1610, 1431, 1398, 1286, 1139, 1043, 923, 819, 723, 584, 520; HRMS (ESI): calc. for $C_{23}H_{16}O_2$ [M + Na]$^+$ 347.1048, found 347.1052.

6,12-Dimethyl-14-*H*-dibenzo[*a*,*c*]xanthen-14-one (2h). White solid. Yield: 74%, M_p: 223.7–226.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (d, $J = 8.3$ Hz, 1H), 8.54 (d, $J = 8.1$ Hz, 1H), 8.45 (d, $J = 8.1$ Hz, 1H), 8.32 (s, 1H), 8.16 (s, 1H), 7.71 (t, $J = 7.5$ Hz, 1H), 7.63–7.59 (m, 1H), 7.52–7.40 (m, 3H), 2.58 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.32, 155.35, 152.63, 140.95, 134.92, 134.44, 133.93, 129.39, 128.94, 128.40, 127.79, 127.25, 126.41, 126.01, 124.01, 123.68, 122.74, 122.29, 121.83, 117.29, 111.94, 22.42, 21.18; IR (KBr), ν (cm^{-1}) 3028, 2914, 1720, 1610, 1429, 1394, 1282, 1033, 919, 806, 524; HRMS (ESI): calc. for $C_{23}H_{16}O_2$ [M + H]$^+$ 325.1229, found 325.1224.

3,6,12-Trimethyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2i). White solid. Yield: 72%, M_p: 254.3–256.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (d, $J = 8.6$ Hz, 1H), 8.41 (d, $J = 8.3$ Hz, 1H), 8.29 (s, 2H), 8.16 (s, 1H), 7.50 (dd, $J = 11.1$, 4.7 Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 2.58 (d, $J = 3.9$ Hz, 6H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.26, 154.83, 152.65, 140.68, 135.97, 134.79, 134.28, 133.69, 129.89, 128.74, 127.62, 127.31, 126.98, 125.97, 123.95, 123.64, 122.67, 122.20, 121.89, 117.28, 111.99, 22.38, 21.92, 21.17; IR (KBr), ν (cm^{-1}) 2914, 1631, 1433, 1402, 1284, 1043, 869, 817, 669, 530; HRMS (ESI): calc. for $C_{24}H_{18}O_2$ [M + H]$^+$ 339.1385, found 339.1375.

3-(*tert*-Butyl)-6,12-dimethyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2j). Yellow solid. Yield: 78%, M_p: 260.2–262.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (d, $J = 8.9$ Hz, 1H), 8.53 (d, $J = 1.6$ Hz, 1H), 8.35 (d, $J = 8.3$ Hz, 1H), 8.29 (s, 1H), 8.11 (s, 1H), 7.80 (dd, $J = 8.9$, 1.9 Hz, 1H), 7.43 (dd, $J = 8.5$, 1.9 Hz, 1H), 7.36 (dd, $J = 8.0$, 4.2 Hz, 2H), 2.57 (s, 3H), 2.46 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.14, 154.87, 152.56, 148.92, 140.63, 134.69, 134.19, 134.04, 128.67, 127.51, 127.02, 126.93, 126.45, 125.88, 123.96, 123.55, 122.43, 121.86, 118.04, 117.22, 111.84, 35.15, 31.64, 22.42, 21.11; IR (KBr), ν (cm^{-1}) 3030, 2952, 1629, 1431, 1402, 1284, 1193, 1039, 850, 808, 659, 536; HRMS (ESI): calc. for $C_{27}H_{24}O_2$ [M + H]$^+$381.1855, found 381.1855.

6-Methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2k). Yellow solid. Yield: 70%, M_p: 185.7–187.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.01 (d, $J = 8.3$ Hz, 1H), 8.38 (d, $J = 8.1$ Hz, 1H), 8.34 (dd, $J = 7.8$, 1.3 Hz, 1H), 8.23 (d, $J = 8.2$ Hz, 1H), 8.13 (s, 1H), 7.66–7.61 (m, 2H), 7.52 (dd, $J = 11.0$, 3.9 Hz, 1H), 7.45 (d, $J = 8.2$ Hz, 1H), 7.38 (t, $J = 7.4$ Hz, 1H), 7.26 (d, $J = 8.2$ Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.05, 155.16, 154.22, 140.90, 133.77, 133.53, 129.11, 128.80, 128.27, 127.66, 127.11, 126.58, 126.34, 124.50, 123.93, 123.78, 122.55, 122.17, 121.47, 117.46, 111.82, 22.34; IR (KBr), ν (cm^{-1}) 3055, 2918, 1633, 1407, 1294, 1112, 1024, 873, 757, 520; HRMS (ESI): calc. for $C_{22}H_{14}O_2$ [M + Na]$^+$ 333.0891, found 333.0893.

3-(*tert*-Butyl)-6-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2l). Yellow solid. Yield: 73%, M_p: 212.2–214.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.06 (d, $J = 8.8$ Hz, 1H), 8.60 (d, $J = 1.8$ Hz, 1H), 8.53 (d, $J = 8.3$ Hz, 1H), 8.45–8.38 (m, 2H), 7.82 (dd, $J = 8.8$, 2.0 Hz, 1H), 7.74–7.69 (m, 1H), 7.60 (d, $J = 8.2$ Hz, 1H), 7.48 (d, $J = 8.2$ Hz, 1H), 7.46–7.41 (m, 1H), 2.65 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.27, 155.14, 154.51, 149.22, 140.94, 134.31, 133.62, 128.88, 127.57, 127.10, 126.97, 126.73, 126.64, 124.57, 124.11, 124.07, 122.66, 121.93, 118.17, 117.58, 112.12, 35.20, 31.64, 22.51; IR (KBr), ν (cm^{-1}) 3099, 2956, 1635, 1463, 1411, 1296, 1122, 1012, 873, 761, 644, 559, 470; HRMS (ESI): calc. for $C_{26}H_{22}O_2$ [M + Na]$^+$ 389.1517, found 389.1516.

2,6-Dimethyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2m). Yellow solid. Yield: 75%, M_p: 218.5–221.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.33 (d, $J = 7.8$ Hz, 1H), 8.23 (t, $J = 8.1$ Hz, 2H), 8.08 (s, 1H), 7.65 (dd, $J = 11.1$, 4.0 Hz, 1H), 7.45 (d, $J = 8.1$ Hz, 1H), 7.38 (t, $J = 7.4$ Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 1H), 7.24 (d, $J = 9.2$ Hz, 1H), 2.54 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.11, 155.29, 154.21, 140.76, 138.21, 133.86, 133.44, 129.12, 128.30, 127.81, 127.39, 126.52, 124.87, 124.44, 123.93, 123.75, 122.32, 122.04, 121.05, 117.44, 111.66, 22.34, 22.16; IR (KBr), ν (cm^{-1}) 3028, 2914, 1637, 1415, 1307, 1172, 1033, 873, 761, 667, 576; HRMS (ESI): calc. for $C_{23}H_{16}O_2$ [M + Na]$^+$ 347.1048, found 347.1048.

11-Methoxy-6-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2n). White solid. Yield: 59%, M_p: 190.2–191.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.15 (d, $J = 8.2$ Hz, 1H), 8.54 (d, $J = 8.2$ Hz, 1H), 8.40 (d, $J = 8.8$ Hz, 1H), 8.32 (s, 1H), 8.27 (d, $J = 8.8$ Hz, 1H), 7.70 (t, $J = 7.4$ Hz, 1H), 7.62–7.60 (m, 1H), 7.41 (d, $J = 8.1$ Hz, 1H), 6.96 (d, $J = 7.4$ Hz, 1H), 6.90 (s, 1H), 3.92 (s, 3H), 2.58 (s, 3H); ^{13}C NMR

(150 MHz, $CDCl_3$) δ 177.70, 164.23, 156.09, 155.24, 140.79, 133.78, 129.43, 128.92, 128.33, 128.09, 127.89, 127.31, 126.38, 123.80, 122.72, 122.27, 121.72, 117.99, 114.04, 111.91, 99.62, 55.95, 22.42; IR (KBr), ν (cm^{-1}) 3016, 2918, 1622, 1444, 1249, 1031, 923, 783, 736, 630, 540; HRMS (ESI): calc. for $C_{23}H_{16}O_3$ $[M + Na]^+$ 341.1178, found 341.1178.

11-Methoxy-2,6-dimethyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2o). Yellow solid. Yield: 70%, M_p: 221.4–223.8 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.46 (d, J = 8.3 Hz, 2H), 8.33 (s, 1H), 8.29 (d, J = 8.8 Hz, 1H), 7.44 (dd, J = 11.3, 8.8 Hz, 2H), 7.01–6.95 (m, 2H), 3.95 (s, 3H), 2.61 (d, J = 8.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.87, 164.25, 156.16, 155.48, 140.77, 138.40, 133.96, 129.50, 128.52, 128.09, 127.96, 127.63, 125.14, 123.85, 122.58, 122.21, 121.37, 118.05, 114.06, 111.83, 99.67, 55.98, 22.45, 22.23; IR (KBr), ν (cm^{-1}) 2912, 1627, 1444, 1257, 1172, 1022, 825, 690, 576, 466; HRMS (ESI): calc. for $C_{24}H_{18}O_3$ $[M + Na]^+$ 377.1154, found 377.1157.

3-(*tert*-Butyl)-11-methoxy-6-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2p). Yellow solid. Yield: 71%, M_p: 205.6–208.1 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 10.07 (d, J = 8.8 Hz, 1H), 8.57 (d, J = 1.6 Hz, 1H), 8.40 (d, J = 8.3 Hz, 1H), 8.36 (s, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.80 (dd, J = 8.8, 1.9 Hz, 1H), 7.40 (d, J = 8.3 Hz, 1H), 6.92 (dd, J = 8.8, 2.3 Hz, 1H), 6.87 (d, J = 2.3 Hz, 1H), 3.89 (s, 3H), 2.61 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.66, 164.11, 156.10, 154.87, 148.98, 140.56, 133.98, 128.73, 128.00, 127.60, 127.09, 127.05, 126.47, 123.84, 122.51, 121.84, 118.04, 117.92, 113.92, 111.88, 99.57, 55.90, 35.17, 31.63; IR (KBr), ν (cm^{-1}) 3095, 2952, 1627, 1409, 1255, 1170, 1033, 921, 825, 688, 557, 474; HRMS (ESI): calc. for $C_{27}H_{24}O_3$ $[M + Na]^+$ 419.1623, found 419.1623.

3-Fluoro-6-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2q). Yellow solid. Yield: 55%, M_p: 267.4–269.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.23–10.14 (m, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.43 (d, J = 7.9 Hz, 1H), 8.28 (s, 1H), 8.20 (d, J = 10.7 Hz, 1H), 7.78–7.75 (m, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.46 (dd, J = 17.2, 9.5 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.16, 161.56 (d, ^1J = 244.92 Hz), 155.08, 154.56, 141.44, 133.95, 133.34 (d, ^4J = 3.87 Hz), 130.38 (d, ^3J = 8.18 Hz), 129.79, 129.58 (d, ^3J = 7.58 Hz), 126.82, 125.77, 124.85, 124.29, 124.04, 123.16, 122.37, 117.65, 116.78 (d, ^2J = 21.72 Hz), 112.00, 107.86 (d, ^2J = 22.17 Hz), 22.46; IR (KBr), ν (cm^{-1}) 3060, 2918, 1934, 1635, 1469, 1411, 1226, 1116, 813, 750, 638, 536; HRMS (ESI): calc. for $C_{22}H_{13}FO_2$ $[M + H]^+$ 329.0978, found 329.0968.

3-Chloro-11-methoxy-6-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2r). White solid. Yield: 58%, M_p: 237.2–239.1 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 10.09 (d, J = 9.0 Hz, 1H), 8.45 (d, J = 2.0 Hz, 1H), 8.42 (d, J = 8.8 Hz, 1H), 8.26 (d, J = 8.8 Hz, 1H), 8.22 (s, 1H), 7.61 (dd, J = 9.0, 2.1 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.00 (dd, J = 8.8, 2.3 Hz, 1H), 6.95 (d, J = 2.2 Hz, 1H), 3.97 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.41, 164.46, 156.14, 155.15, 141.23, 132.64, 132.62, 129.61, 129.53, 128.80, 128.50, 128.15, 127.72, 123.92, 122.81, 122.13, 121.94, 117.86, 114.25, 111.54, 99.72, 56.03, 22.41; IR (KBr), ν (cm^{-1}) 2920, 1627, 1444, 1407, 1253, 1164, 1037, 906, 821, 759, 686, 538; HRMS (ESI): calc. for $C_{23}H_{15}ClO_3$ $[M + H]^+$ 375.0788, found 375.0783.

3-Fluoro-6-methoxy-12-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2s). White solid. Yield: 64%, M_p: 253.4–256.1 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.52 (d, J = 8.3 Hz, 1H), 8.16 (s, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.75 (s, 1H), 7.46 (dd, J = 31.1, 24.0 Hz, 3H), 7.25 (s, 1H), 4.02 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.90, 161.41 (d, ^1J = 244.71 Hz), 161.86, 154.94, 152.79, 135.03, 134.96, 134.58, 130.52 (d, ^3J = 7.88 Hz), 129.10 (d, ^4J = 3.74 Hz), 126.33, 126.16 (d, ^4J = 4.86 Hz), 123.71, 118.62, 117.69, 117.26, 116.85 (d, ^2J = 21.81 Hz), 110.92, 107.72 (d, ^2J = 21.99 Hz), 104.89, 55.73, 21.15; IR (KBr), ν (cm^{-1}) 3105, 2964, 1917, 1610, 1458, 1234, 1026, 813, 636, 536; HRMS (ESI): calc. for $C_{23}H_{15}FO_3$ $[M + H]^+$ 359.1083, found 359.1089.

3-Fluoro-11-methoxy-6-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2t). White solid. Yield: 55%, M_p: 220.3–222.1 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.21 (dd, J = 9.4, 6.3 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.26 (s, 1H), 8.18 (dd, J = 10.9, 2.6 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.47–7.40 (m, 1H), 7.04–6.99 (m, 2H), 3.98 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.57, 164.46, 161.86, 161.46 (d, ^1J = 224.65 Hz), 156.24, 141.07, 133.03 (d, ^4J = 3.92 Hz), 130.44 (d, ^3J = 8.09 Hz), 129.64, 129.50 (d, ^3J = 8.03 Hz), 128.21, 125.89 (d, ^4J = 1.74 Hz), 124.02, 123.04, 122.29, 117.96, 116.62 (d, ^2J = 21.78 Hz), 114.22, 111.81, 107.71 (d, ^2J = 22.50 Hz), 99.76, 56.03, 22.41; IR (KBr), ν (cm^{-1}) 2911, 1627, 1448, 1409, 1255, 1109, 950, 819, 538; HRMS (ESI): calc. for $C_{23}H_{15}FO_3$ $[M + H]^+$ 359.1083, found 359.1083.

12-Fluoro-2,6-dimethyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2u). White solid. Yield: 54%, M_p: 222.4–224.1 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.42 (d, J = 8.4 Hz, 2H), 8.30 (s, 1H), 8.00 (dd, J = 8.5, 3.1 Hz, 1H), 7.57 (dd, J = 9.1, 4.1 Hz, 1H), 7.45–7.40 (m, 3H), 2.60 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.42, 159.45 (d, ^1J = 243.59 Hz), 155.72, 150.60, 141.28, 138.64, 134.25, 129.02, 128.64, 128.21, 127.49, 125.15, 125.05 (d, ^3J = 7.18 Hz), 123.98, 122.63, 122.26, 121.79 (d, ^2J = 25.51 Hz), 121.14, 119.53 (d, ^3J = 7.89 Hz), 111.46 (d, ^2J = 23.85 Hz), 111.26, 22.46, 22.21; IR (KBr), ν (cm^{-1}) 3080, 2916, 1895, 1635, 1485, 1272, 817, 655, 541; HRMS (ESI): calc. for $C_{23}H_{15}FO_2$ $[M + H]^+$ 343.1134, found 343.1134.

3-(*tert*-Butyl)-12-fluoro-6-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2v). Yellow solid. Yield: 63%, M_p: 240.2–241.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.95 (d, J = 8.9 Hz, 1H), 8.55 (d, J = 1.5 Hz, 1H), 8.40 (d, J = 8.3 Hz, 1H), 8.35 (s, 1H), 7.97 (dd, J = 8.5, 3.0 Hz, 1H), 7.80 (dd, J = 8.9, 1.8 Hz, 1H), 7.50 (dd, J = 9.0, 4.1 Hz, 1H), 7.45–7.35 (m, 2H), 2.63 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.25, 159.35 (d, ^1J = 243.61 Hz), 155.15, 150.57, 149.38, 141.13, 134.31, 128.89, 127.48, 127.10, 126.69, 126.61, 124.94 (d, ^3J = 7.19 Hz), 124.01, 122.63, 121.68 (d, ^2J = 25.36 Hz), 121.64, 119.49 (d, ^3J = 7.87 Hz), 118.17, 111.43 (d, ^2J = 23.58 Hz), 111.35, 35.21, 31.63, 22.51; IR (KBr), ν (cm^{-1}) 3045, 2954, 1633, 1450, 1263, 1122, 1033, 813, 777, 543; HRMS (ESI): calc. for $C_{26}H_{21}FO_2$ $[M + Na]^+$ 407.1423, found 407.1418.

6-Fluoro-11-methoxy-2-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2w). Yellow solid. Yield: 65%, M_p: 254.4–257.2 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.61 (dd, J = 9.0, 5.9 Hz, 1H), 8.31 (dd, J = 14.5, 8.6 Hz, 2H), 8.16 (dd, J = 11.0, 2.0 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.39–7.33 (m, 1H), 7.01 (dd, J = 13.4, 4.6 Hz, 2H), 3.97 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.68, 164.43, 164.26 (d, ^1J = 248.98 Hz), 156.14, 154.84, 139.41, 136.11 (d, ^3J = 9.15 Hz), 128.25, 128.19, 127.78, 126.78

(d, $^3J = 9.37$ Hz), 124.64 (d, $^4J = 3.72$ Hz), 122.47, 120.21, 117.98, 115.81 (d, $^2J = 23.56$ Hz), 114.23, 111.9537, 111.9448, 108.21 (d, $^2J = 22.61$ Hz), 99.72, 56.02, 22.25; IR (KBr), ν (cm^{-1}) 2974, 1897, 1623, 1417, 1271, 1166, 1051, 821, 607, 430; HRMS (ESI): calc. for $C_{23}H_{15}FO_3$ $[M + H]^+$ 359.1083, found 359.1083.

3-(*tert*-Butyl)-6-fluoro-11-methoxy-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2x). White solid. Yield: 69%, M_p: 254.2–256.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (d, $J = 8.9$ Hz, 1H), 8.47 (dd, $J = 8.9$, 6.0 Hz, 1H), 8.38 (s, 1H), 8.22 (d, $J = 8.9$ Hz, 1H), 8.18–8.11 (m, 1H), 7.85–7.77 (m, 1H), 7.26 (d, $J = 6.6$ Hz, 1H), 6.92 (dd, $J = 8.9$, 2.0 Hz, 1H), 6.83 (s, 1H), 3.90 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.43, 164.26, 164.03 (d, $^1J = 248.80$ Hz), 156.04, 154.14, 149.38, 136.03 (d, $^3J = 8.78$ Hz), 128.04, 127.72, 127.31, 126.66 (d, $^3J = 9.28$ Hz), 126.48 (d, $^4J = 3.55$ Hz), 120.56, 118.26, 117.79, 115.89 (d, $^2J = 23.63$ Hz), 114.11, 111.95, 108.18 (d, $^2J = 22.75$ Hz), 99.56, 55.94, 35.18, 31.56; IR (KBr), ν (cm^{-1}) 3099, 2960, 1625, 1442, 1255, 1166, 1035, 941, 827, 734, 578, 478; HRMS (ESI): calc. for $C_{26}H_{21}FO_3$ $[M + H]^+$ 401.1553, found 401.1562.

3-(*tert*-Butyl)-11-hydroxy-6-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2y). Red solid. Yield: 78%, M_p: 291.6–293.4 °C. ^{1}H NMR (600 MHz, DMSO) δ 10.75 (s, 1H), 9.83 (d, $J = 8.1$ Hz, 1H), 8.56 (s, 2H), 8.43 (d, $J = 8.2$ Hz, 1H), 7.98 (d, $J = 8.6$ Hz, 1H), 7.66 (d, $J = 8.8$ Hz, 1H), 7.47 (d, $J = 8.1$ Hz, 1H), 6.97 (s, 1H), 6.85 (d, $J = 8.6$ Hz, 1H), 2.37 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (150 MHz, DMSO) δ 176.37, 162.97, 155.74, 154.08, 148.71, 140.91, 133.12, 129.11, 127.64, 126.69, 126.56, 126.34, 125.96, 123.59, 122.80, 121.10, 118.47, 116.05, 114.70, 110.60, 101.83, 34.78, 31.22, 21.67; IR (KBr), ν (cm^{-1}) 3189, 2958, 1620, 1415, 1269, 1174, 923, 821, 559, 468; HRMS (ESI): calc. for $C_{26}H_{22}O_3$ $[M + Na]^+$ 405.1467, found 405.1463.

6-Hydroxy-12-methyl-14*H*-dibenzo[*a*,*c*]xanthen-14-one (2z). White solid. Yield: 70%, M_p: 299.4–301.2 °C. ^{1}H NMR (600 MHz, DMSO) δ 10.62 (s, 1H), 10.04 (d, $J = 8.3$ Hz, 1H), 8.63–8.59 (m, 2H), 8.07 (d, $J = 1.8$ Hz, 1H), 8.01 (s, 1H), 7.74–7.70 (m, 2H), 7.68–7.63 (m, 2H), 7.33 (dd, $J = 8.9$, 2.1 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 176.84, 160.51, 155.20, 152.07, 135.61, 135.20, 134.28, 128.92, 128.36, 126.81, 126.44, 126.40, 126.20, 125.03, 122.80, 122.79, 118.15, 117.55, 116.00, 109.31, 107.12, 20.55; IR (KBr), ν (cm^{-1}) 3145, 2912, 2314, 1608, 1436, 1244, 806, 619, 526; HRMS (ESI): calc. for $C_{22}H_{14}O_3$ $[M + Na]^+$ 349.0841, found 349.0839.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

We are grateful for financial support from the National Natural Science Foundation of China (No. 21672132, 21502110).

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